

Stability of quasi-two dimensional zigzag carbon and its reaction pathway to graphene

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Using the density functional theory we investigate a quasi-two dimensional carbon allotrope, ZzC, formed by square carbon lattice buckled in zigzag manner. By analyzing the Kohn-Sham energy and phonon dispersion obtained by lattice dynamical calculations we show that ZzC is stable with binding energy of 7.46 eV per atom. To examine the possible route of formation we find out reaction pathway from ZzC to graphene using nudge elastic band method, generalized for solid state calculations. The reaction pathway shows the formation of carbyne as the intermediate state. Such a pathway is seen to exhibit two transition states with reaction barriers of 0.21 eV/atom from ZzC to carbyne, and of 1.19 eV/atom from graphene to carbyne. Although ZzC is stable, upon hydrogenation it dissociates and prefers the carbyne-like structure by forming chains of polyacetylene.

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I. INTRODUCTION

Variety of *sp* hybridizations of carbon allows it to have diversity of structures in all three dimensions¹. After discovery of graphene, 2D family of carbon allotropes became subject of special interest. For example, hydrogenated graphene, called as *graphane* is under investigation by both theoretical and experimental groups²⁻⁹. Other materials like graphone and graphYn have also been predicted theoretically. Zhou *et al*¹⁰ showed that semihydrogenated graphone can act as a ferromagnetic material. On the other hand graphyne has been claimed to be better than graphene¹¹⁻¹³. An exhaustive theoretical study was carried out recently by Wen *et al*¹ who investigated various allotropes of Group 14 elements using Density functional theory (DFT). They studied a variety of 1D, 2D and 3D structures of group IV elements; particularly their geometries and stabilities by means of formation energies. Their extensive study shed the light on various structures and their relative stability. They also found that in 2D a wavy square sheet of carbon is considerably more stable than other crystals except graphene. It thus becomes very intriguing to investigate such wavy material in details, which we call Zigzag carbon (ZzC).

In this work we investigate the crystal structure, stability and electronic structure of ZzC. The relative stability is investigated by using binding energy (BE) and phonon dispersion spectra as BE cannot be considered conclusive. Moreover, we also investigate the reaction pathway from ZzC to graphene. Such a transition involves both atomic and cell degrees of freedom. We address this transition using Linear Synchronized Transit (LST), Quadratic Synchronized Transit (QST)¹⁴ and Generalized Solid-State Nudge Elastic Band (G-SSNEB)¹⁵ methods. Although LST is easy to implement, QST, and specially G-SSNEB are more accurate in predicting transi-

tion state. We observed that QST reaction barrier from ZzC to carbyne is in 5% in agreement with G-SSNEB one.

II. COMPUTATIONAL DETAILS

We perform constraint free full unit cell optimization using Generalized Gradient Approximation (GGA) with exchange correlation functional of Perdew, Burke and Ernzerhof¹⁶ as implemented in Quantum ESPRESSO¹⁷. The primitive cell contains two carbon atoms. The unit cell optimization was terminated upon reaching the pressure cut-off of 0.1 Kbar. Kinetic energy cutoff on plane waves was set to as high as 1360 eV. The energy criterion for electronic self consistency was set to 10^{-8} eV while that for structural optimization was 10^{-7} eV. For the optimization the *k*-mesh was sampled using $16 \times 16 \times 1$ points using Monkhorst-Pack scheme, while the band structure was plotted on lines joining four symmetry points of Wigner-Seitz cell, and the individual line segments were sampled using fifty *k*-points. A vacuum space of 25 Å was kept normal to the plane to avoid any inter-planar interactions.

Phonon dispersion is obtained by lattice dynamical calculations performed using self-consistent density functional perturbation theory within linear response approach. The energy threshold value for convergence was 1.4×10^{-15} eV. Force constant matrices are obtained on a $3 \times 3 \times 1$ *k*-point mesh of irreducible part of Brillouin zone, and are interpolated at arbitrary wave vectors. The dispersion spectrum is then plotted along the lines joining symmetry points sampled using total of 150 *q* points.

For finding solid-state transition pathway between graphene and ZzC we used three methods: LST, QST and G-SSNEB. In LST all degrees of freedom (DOF), namely cell parameters and atomic positions, are varied linearly from reactants to products. The maximum on the resulting pathways corresponds to a transition state (TS). Better results of TS are obtained by QST,

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in which one should first optimize the LST maximum orthogonally to its pathway in combined phase space of coordinates and cell vectors. (In this work we finally changed orthogonal optimization to unrestricted optimization because the resulting structure appeared to be another carbon allotrope with energy below ZzC.) Then a quadratic transit pathway is built from reactants to products through this TS. For detailed discussion on QST we refer reader to reference 14. The G-SSNEB method, which we implemented in QE, was developed by Henkelmann's group¹⁵. The only difference with original method is the cell gradient (Eq.(2)), which we used in the form given by Caspersen and Carter.¹⁸ Choice of gradient is based on ease of numerical implementation and although the nature of gradients are different in both the cases; we believe that they should produce identical results in a simple case that we are studying.

The gradient in the combined phase space is the generalized forces, which are

$$-\frac{\partial E}{\partial \mathbf{x}} = \mathbf{F} \cdot \mathbf{h}^T \quad (1)$$

$$-\frac{\partial E}{\partial \mathbf{h}} = -\Omega \left((\sigma + P\mathbf{I}) \cdot \mathbf{h}^{-1} \right)^T \quad (2)$$

where \mathbf{x} , \mathbf{F} , \mathbf{h} , σ are matrices of atomic positions in crystal coordinates, forces, cell vectors and internal Cauchy stress tensor accordingly. P is the external pressure, equaled zero in our calculations.

III. RESULTS AND DISCUSSION

We shall begin the discussion by the presenting the lattice structure and the stability, and proceed to electronic structure and the reaction pathway from ZzC to graphene. We shall also talk about the effect of hydrogenation.

A. Crystal: structure and stability

Figure 1(a) shows the optimized crystal structure along with its lattice parameters and bond lengths. For sake of clarity various views are depicted, which also make the name zigzag carbon evident. The unit cell belongs to C_{2h} point group of monoclinic crystal, with lattice parameters of $a = 2.46$ Å, $b = 1.65$ Å. As seen from the top view the bond length along the zigzag direction (1.51 Å) is smaller than that along non-zigzag direction (1.65 Å). These numbers are consistent with Wen *et al*¹ (1.50 and 1.63 Å respectively; bearing in mind the choice of different treatment on exchange correlation functional). At this point we recall that the C-C bond length is 1.42 Å and 1.62 Å in graphene and SqC (planar square carbon allotrope¹⁹) respectively. It is thus intuitive to think that binding energy of ZzC may lie in between the two. Indeed, ZzC has the binding energy of 7.46 eV per atom

which is higher than SqC (6.7 eV per atom) but not as high as graphene (9.6 eV per atom). However binding energy alone cannot serve as the stability criterion. The stability of ZzC becomes evident conclusively by analysing the phonon dispersion spectrum (Figure 1(b)). Obviously, the lack of any imaginary phonons in entire Brillouin zone strongly underlines the stability of ZzC. The phonon spectrum has total of six branches, three acoustic and three optical (out-of-plane, in-plane transverse and in-plane longitudinal for both types). It is interesting to note that although there is no band gap between acoustic and optical branches, an indirect band gap of 18.9 cm^{-1} exists between the out-of-plane optical mode and in-plane transverse optical mode. Thus, from phonon dispersion it becomes evident that ZzC is indeed a stable material with a high binding energy.

B. Electronic structure

After validating the stability we now discuss the electronic structure of ZzC. As seen from the band structure (Figure 2(a)) ZzC shows a small band gap of 0.39 eV at the X' point of Brillouin zone. The band gap at Γ point is rather high (7.8 eV). We also note that ZzC does not show any magnetic character. Figure 2(b) also shows the charge densities of highest occupied and lowest unoccupied bands. Highest occupied band which is primarily p -type shows the stacking of baguette-shaped charge density, while unoccupied band completely embed the atoms within individual planes. It is interesting to note that both states show the delocalization perpendicular to the zigzag direction. Looking at the delocalized nature of bands and bearing in mind that DFT tends to underestimate the band gap, one may speculate that the ZzC may act as a semiconductor with peculiar conductance perpendicular to zigzag direction.

C. Reaction pathway

LST, QST and G-SSNEB pathways along with initial, transition, intermediate and final states, are presented in Figure 3. LST method does not have the intermediate state found by QST and G-SSNEB independently. It is explained by non-iterative nature of LST: it represents only the shortest pathway between reactant and product, and is useful only as a quick and rough approximation. Presence of the intermediate state, carbyne (weakly binded carbon chains), means a multistep reaction: along the pathway to the more stable graphene allotrope ZzC dissociates to carbyne. Carbyne structure (Figure 3) is composed of linear carbon chains²⁰ weakly binded by dispersion interaction. Our results are in good agreement with parameters of betta-carbyne (or polycumulene type, cumulated double bonds) in Heinmann's work²¹. In particular double C=C bond is equal 1.28 Å in both cases, which is in agreement with the Steichen's

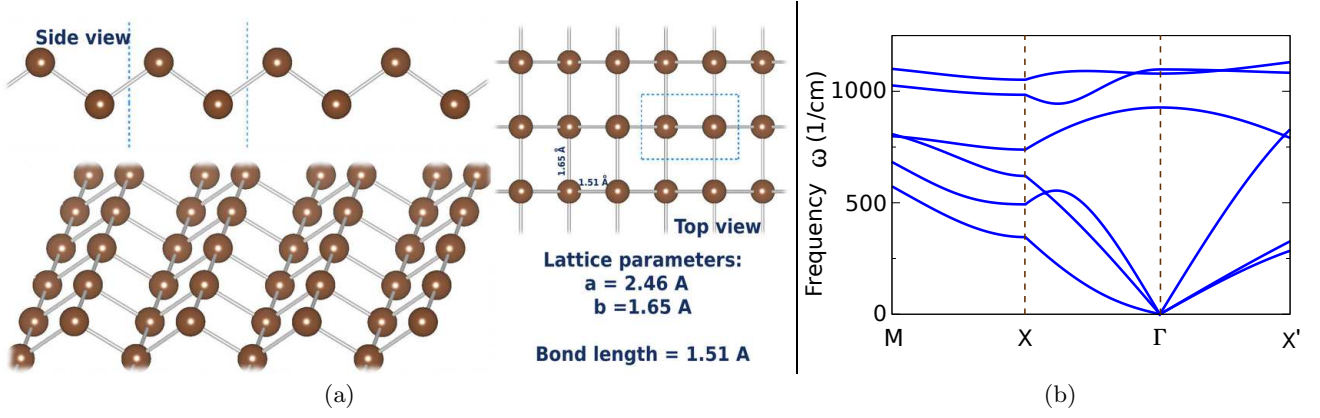


FIG. 1. (a) Optimized structure of ZzC. The name zigzag is evident from the side view. The dotted blue line indicate the primitive unit cell which has the parameters $a = 2.46 \text{ Å}$, $b = 1.65 \text{ Å}$ and $\gamma = 90^\circ$. The primitive cell has two carbon atoms with the bond length of 1.51 Å . (b) The phonon dispersion relation is shown along the symmetry points of Brillouin zone. The absence of soft modes confirms the stability.

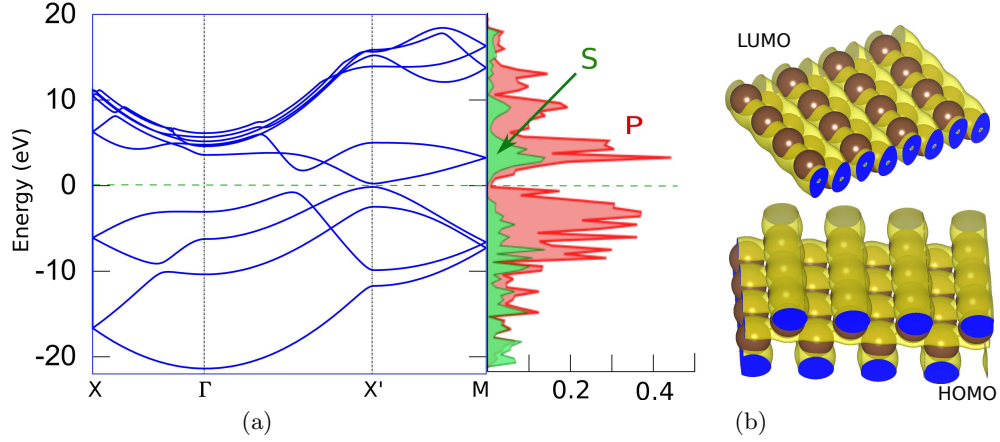


FIG. 2. (a) Band structure and the DOS of ZzC. DOS are resolved as per their angular momentum components (s and p) and are plotted using the electronic smearing of 0.1 eV for better visualization. A small band gap of 0.39 eV is seen at the X' point. (b) Charge density of highest occupied and lowest unoccupied bands show the decolocalization perpendicular to zigzag direction.

principle²². Interchain distances are 3.7 and 2.9 Å in our and Heinmann's work accordingly. The bigger value in our case is due to different unit cells in the works. In our calculation we used artificially small unit cell for carbyne: there are only two carbon atoms, whereas in Heinmann's work n -atoms cells ($n \gg 2$) are presented. Bigger cell allows more energetically favourable packing, which leads to higher interaction, thus smaller interchain distance. That difference also explains different transition temperatures from graphene to carbyne: in our calculation reaction barrier from graphene to carbyne is 1.19 eV/atom , that corresponds to about 4600 K (the method of temperature calculation is described in the next paragraph), whereas in the work of Nelson etc.²³ graphene was heated above 2600 K . The planar structure of car-

byne is most likely an artefact caused by construction of primitive cell (to consider possibility of non-planar structure supercell in the orthogonal direction to the chains should be constructed). In reality final structure could be a layer or even clusters of amorphous carbon composed of crosslinked linear chains^{20,24}. But this part of modeling lies beyond the scope of this article.

To answer the question of stability of ZzC structure we calculated transition temperature corresponding to reaction barrier using rough approximation of atoms as independent simple harmonic oscillators having energy $3kT$ each. Thus, a rough value of the transition temperature is $E/(3k)$, where E and k are energy of reaction barrier per atom and Boltzmann constant accordingly. For transition from ZzC to carbyne it corresponds to

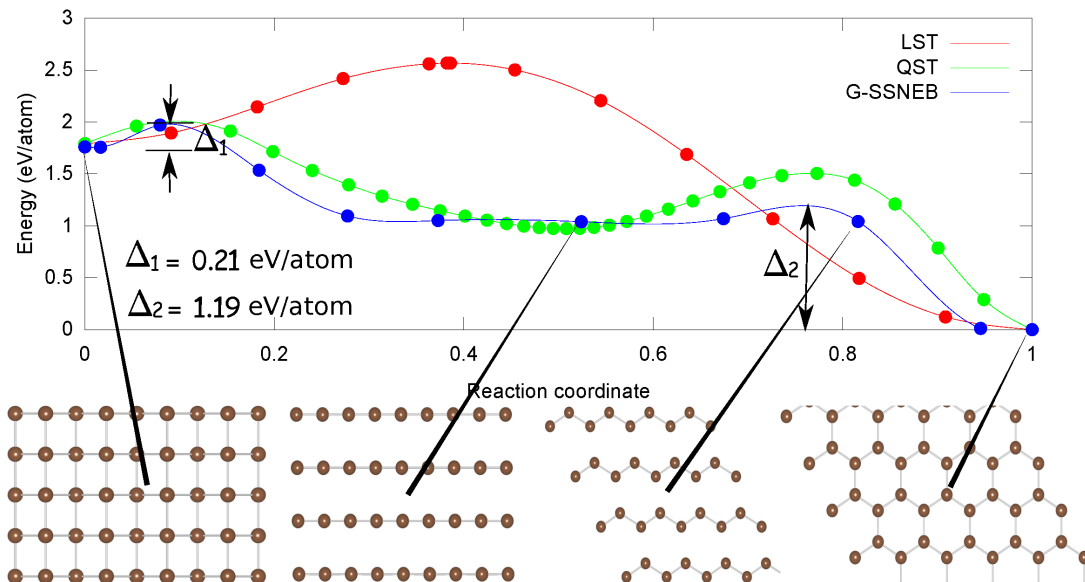


FIG. 3. Reaction pathways from ZzC to graphene using LST, QST and G-SSNEB methods (in the last one we used two climbing images because of two reaction barriers).

around 815 K. Thus ZzC structure is a pretty stable composition.

D. Hydrogenation

At this stage we wish to point out an interesting observation. Unlike graphene or SqC¹⁹, ZzC responds to hydrogenation in qualitatively different manner. We recall that upon hydrogenation graphene forms *graphane*, while SqC accommodates hydrogens by forming hexacoordinated bonds. In contrast, we observed that upon hydrogenation, ZzC breaks down and forms stacks of polyacetylene ($[-CH]_n$). The individual chains of polymers were spatially separated by more than 3.5 Å, ruling out the van der Waals interactions. We verified the absence of any such interactions by enabling a correction term to the exchange correlation functional, to take into account the long range the dispersion.^{25,26} Yet, such different response to hydrogenation is understandable by analyzing the nature of electronic structure. While graphene has one double bond, SqC has electron deficient bonding. On

the other hand, all bonds in ZzC are single bonds and are completely saturated. By disintegrating into polyacetylene carbon atoms gain significant binding energy (from 7.46 eV to 8.31 eV per atom). Thus although the ZzC is extremely stable, we speculate that it can be easily converted into stacks of polyacetylene by hydrogenation.

IV. CONCLUSIONS

We performed the full unit cell optimization on zigzag carbon and found out that the ZzC may act as the semiconductor with valance and conductance bands peculiarly delocalized only perpendicular to the zigzag direction. Our calculations revealed that with binding energy of 7.46 eV per atom ZzC is stable, which we also verified using lattice dynamical calculations. We also observed that ZzC breaks into chains of polyacetylene upon hydrogenation. Finally our reaction path from ZzC to graphene using QST and G-SSNEB showed that ZzC transforms into carbyne with reaction barrier 0.21 eV/atom, roughly corresponding 815 K transtion temperature. We believe many other exotic 2D carbon allotropes have the same fate: breaking apart to carbon chains with following amorphous phase formation.

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